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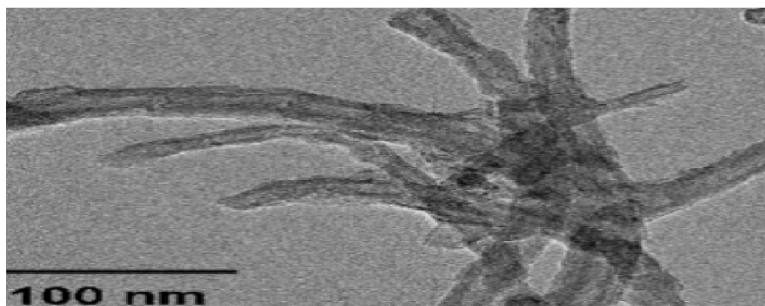
Article

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Cross-Linking of Multiwalled Carbon Nanotubes with Polymeric Amines

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ABSTRACT: Functionalization of carbon nanotubes is considered as an essential step to enable their manipulation and application in potential end-use products. In this paper we introduce a new approach to functionalize multiwalled carbon nanotubes (MWNTs) by applying an amidation-type grafting reaction with amino-functionalized alternating polyketones. The functionalized MWNTs were characterized by using thermogravimetric analysis (TGA), X-ray photoemission spectroscopy (XPS), element analysis, Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Around 40 wt % polyamines based on the total weight of the MWNTs can be covalently attached to the surface of the MWNTs. It is found that polyamines act as cross-linking agents to interconnect or cross-link the MWNTs within and between bundles, as demonstrated by SEM and TEM analysis. After cross-linking, the functionalized MWNTs are insoluble in any solvent. The cross-linked MWNTs can be melt-blended into polyethylene, and the resulting composites show comparable mechanical properties to those obtained by simple blending of “un-cross-linked” nanotubes with polyethylene.

Introduction

Carbon nanotubes have attracted great research interest because of their unique structural, mechanical, and electrical properties.¹ Functionalization of carbon nanotubes via noncovalent adsorption, wrapping of various functional molecules, or covalent attachment of chemical groups is essential to facilitate their manipulation (e.g., dispersion of carbon nanotubes in various solvents) for many further applications.^{2–4} It has been shown that carbon nanotubes can be dispersed in aqueous media or organic solvents via noncovalent adsorption of low molecular weight surfactants⁵ and polymers^{6–8} (such as diblock copolymers and amphiphilic polymers). The covalent functionalization with organic molecules is mostly achieved by exploiting the reactivity of carbon nanotube-bound carboxylic acids via amidation or esterification reactions.^{9–11} The carboxylic acid groups can be obtained on the surface of the nanotubes by oxidation (usually from intrinsic or induced surface defects). In terms of polymer systems, the so-called “grafting onto” (attaching polymers with reactive or functional groups onto carbon nanotubes) and “grafting from” (growing polymers from carbon nanotube surfaces by in situ polymerization) approaches are applied to functionalize carbon nanotubes.^{12–15}

Some chemical functionalization using bifunctional molecules enable the interlinking or cross-linking of individual carbon nanotubes to form carbon nanotube junctions or complex networks for the application as nanoscale electronic circuits.^{16,17} The first interconnection (e.g., end-to-end and end-to-side heterojunctions) of single wall carbon nanotubes (SWNTs) has been achieved by using aliphatic diamines as linkers via amide linkages.^{17–19} Using a cycloaddition reaction, SWNTs can be cross-linked within a bundle as well as between bundles by using bifunctional nitrenes.²⁰ With respect to multiwalled carbon

nanotubes (MWNTs), it has been reported that interconnects of MWNTs can be formed through amide linkage with an inorganic metal complex.²¹ Alternative ways for cross-linking of carbon nanotubes include the use of electron or ion-beam irradiation.^{22–25} Introducing cross-links between the carbon nanotube bundles could lead to dramatic improvement in mechanical strength,^{26,27} since the mechanical properties of nanotube bundles after production are limited by the sliding of individual carbon nanotubes along each other because of the relatively weak van der Waals interaction between them. Here we report the use of a polymeric component to create, via the amidation reaction, cross-linking points within or between the bundles of MWNTs. On the basis of the “grafting onto” approach, chemical cross-linking of MWNTs was carried out by using amino-functionalized alternating polyketones as the polymeric component.

The polymeric amines (polyamines) used for this study were first prepared by chemical modifications of aliphatic alternating polyketones via the Paal–Knorr reaction.²⁸ XPS, element analysis, TGA, and Raman spectroscopy were employed to characterize the functionalized MWNTs. The presence of polymer linkage between carbon nanotubes was examined with TEM and SEM. Furthermore, LDPE/cross-linked MWNTs composites were prepared using a twin-screw microextruder, and the morphology and mechanical properties of the composites were investigated. The use of polymers for the cross-linking of carbon nanotubes has not been reported before. We believe this research can open up new approaches for the preparation of carbon nanotube interconnects.

Experimental Section

Materials. MWNTs (>90%) produced by CVD (chemical vapor deposition) were purchased from Aldrich with outer diameter 10–15 nm, inner diameter 2–6 nm, and length 0.1–10 μm . The alternating polyketones (M_w 3970), ter-polymers of carbon monoxide, ethene, and propene were synthesized according to a reported procedure.²⁹ 1,2-Diaminopropane (1,2-DAP, Acros), thionyl chloride (Fluka), nitric acid (Merck, 65%), THF (Acros, >99%), toluene (Laboratory-

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Scan, 99.5%), chloroform (Laboratory-Scan, 99.5%), and DMF (Acros, >99%) were purchased and used as received. Anhydrous THF and toluene (Aldrich, anhydrous, 99.8%) for the functionalization of MWNTs were dried over Al_2O_3 (Fluka). Anhydrous solvents were degassed prior to use and stored under nitrogen. The low-density polyethylene (LDPE) in this study was purchased from Aldrich with a melt index 25 g/10 min (190 °C/2.16 kg) and density 0.925 g/mL at 25 °C.

Preparation of the Polyamines. Polyamines were prepared in bulk by reacting two components (polyketones and 1,2-DAP) in a one-pot synthesis at 100 °C for 4 h. After reaction, the resulting mixtures were washed several times with deionized Milli-Q water. After filtering and freeze-drying, light brown polymers were obtained as final products. Details of the procedure and characterization of the prepared polyamines were reported elsewhere.²⁸

Chemical Functionalization of MWNTs. MWNTs (3 g) were added to 65% HNO_3 aqueous solution (100 mL). The mixture was first treated in an ultrasonic bath (Bransonic 2510) for 30 min and then stirred for 24 h under reflux. After cooling down to room temperature, the resulting mixture was diluted with 200 mL of deionized water and vacuum-filtered through 0.2 μm polycarbonate membrane. The obtained solid was washed with deionized water until the pH of the filtrate was 7. After drying overnight under vacuum at 60 °C, a solid (MWNTs-COOH, 1.65 g) was obtained. MWNTs-COOH (0.5 g) was suspended in thionyl chloride (40 mL). The mixture was stirred for 24 h under reflux, followed by the removal of excess thionyl chloride under vacuum, giving acyl chloride-functionalized MWNTs (MWNT-COCl). The MWNT-COCl was washed with anhydrous THF (20 mL), and the excess THF was removed under vacuum. The polyamines (6.5 g) were first dissolved in anhydrous toluene (40 mL) at room temperature. Then the dissolved polyamines in toluene were added into MWNT-COCl (0.45 g). The reaction mixture was first sonicated for 30 min at room temperature and then vigorously stirred at 90 °C under a nitrogen atmosphere for the reaction time of 30 h. After the reaction was finished, the entire mixture was centrifuged at 3000 rpm for 10 min. The functionalized MWNTs in the mixture after centrifuging were all precipitated at the bottom of the glass vial, and the upper solvent layer containing the excess polyamines was carefully decanted. The resulting solid (MWNTs-PA) were repeatedly washed with toluene and centrifuged for 4–5 cycles to remove the unreacted polyamines from the surface of the carbon nanotubes and then again washed with THF for 3–4 cycles to ensure complete removal of excess polyamines. The final product (MWNTs-PA) (0.74 g) was obtained by the removal of the solvent under vacuum.

Blends with Polyethylene. The LDPE was melt-blended with pristine MWNTs and MWNTs-PA (1–6 wt %) using a 5 cm^3 microextruder (DSM Research Products B.V., The Netherlands) with barrel temperature of 150 °C and a screw speed of 160 rpm for 10 min. The extruder operated with two corotating conical screws and was of the self-wiping type. The mixed samples were then compressed into the specimens (length 22 mm, width 4.7 mm, thickness 0.75 mm) with dog-bone shape under a pressure of about 8 MPa at 150 °C for 10 min using a hot press. Thin films of the composites were also prepared using hot press in order to study the dispersion of carbon nanotubes in the LDPE with a Zeiss Axiophot microscope equipped with a Plan-NEOFLUAR 20 \times /0.45 objective.

Characterization. Thermal gravimetric analysis (TGA) was conducted in a nitrogen environment on a Perkin-Elmer TGA 7 instrument from 20 to 800 °C at a heating rate of 10 °C/min. Element analysis of C, H, and N was performed with an Euro EA elemental analyzer. X-ray photoemission spectroscopy (XPS) measurements were performed with an SSX-100 (Surface Science Instruments) photoemission spectrometer with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). A suspension of the MWNTs in ethanol was drop-cast on a polycrystalline gold substrate. The base pressure in the spectrometer was 1×10^{-10} Torr. The energy resolution was set to 1.3 eV to minimize the data acquisition time, and the photoelectron takeoff angle was 37°. Raman spectra, excited by the second harmonic light of a Nd:YVO4 laser (532 nm), were

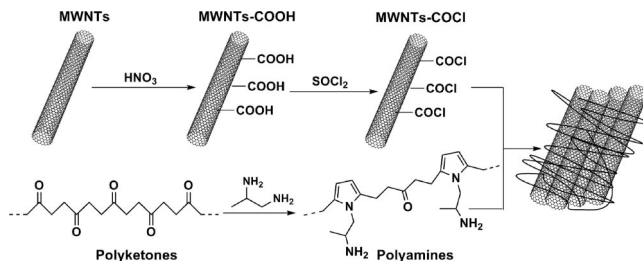


Figure 1. Schematic illustration of the functionalization of MWNTs with the polyamines.

recorded on a micro-Raman spectrometer (T64000 Jobin Yvon) equipped with a liquid nitrogen-cooled charged coupled device (CCD) detector. Scanning electron microscopy (SEM) was carried out on a JSM-6320 instrument with an accelerating voltage of 2 kV, and the samples were sputtered with Pt/Pd prior to SEM observation. Transmission electron microscopy (TEM) micrographs were recorded on a Philips CM 120 electron microscope operating at 120 kV. After 30 min sonication, one drop of the MWNTs suspension in water was placed on a glow discharged carbon-coated grid and followed by the evaporation of the solvent for the TEM examination. Tensile properties of the LDPE/MWNTs composites were tested on an Instron 5565 machine using 0.1 kN power sensor at a crosshead rate of 10 mm/min. The tensile fracture surface of the composites after mechanical testing were examined by SEM.

Results and Discussion

Grafting of Polyamines onto MWNTs. Our approach to the cross-linking of MWNTs with polyamines is illustrated in Figure 1. The used polyamines, which have N-substituted 2,5-pyrrolediyl groups incorporated in the backbone with an amino functional group pendant from the main chain, were synthesized by reacting the polyketones with 1,2-DAP. Because of the steric effect of the 1,2-DAP, only the nonsterically hindered amino group (position 1 in 1,2-DAP) could react with 1,4-dicarbonyl unit of the polyketones, and the other one (position 2 in 1,2-DAP) remains intact as functional group. After modification, around 70% of the carbonyl groups of the polyketones have been converted into pyrrole units bearing a primary amino group in the β -position with respect to the nitrogen atom on the pyrrole ring. Carboxylic acid-functionalized MWNTs (MWNTs-COOH) were obtained by the oxidation reaction of MWNTs with the concentrated HNO_3 . It has been reported that the carbon bonds at the open ends and at defects side of the side walls of the carbon nanotubes could be terminated with carboxylic acid groups after the strong acid treatment.^{30–32} These functional groups attached to the nanotubes can be converted into the corresponding acyl chlorides (MWNTs-COCl) by treatment with thionyl chloride. The acyl chloride functions are then susceptible to react with the amino groups of the polyamines (yielding amide linkages) to produce the interlinked MWNTs with polyamines (MWNTs-PA). This is similar, in terms of the used chemistry, to earlier work on the chemical functionalization of carbon nanotubes with aliphatic diamines.¹⁷

The TGA spectrum of MWNTs-PA (Figure 2a) exhibited a main weight loss between 200 and 450 °C, which can be attributed to thermal degradation of the attached polyamines since it mirrors the weight loss behavior of pure polyamines. Pristine MWNTs show no weight loss up to 800 °C, and MWNTs-COOH has a weight loss $\sim 13\%$. The noticeable slight increase in weight loss as compared to MWNTs-COOH and polyamines in the temperature range 100–200 °C is due to the small amount of residual solvent (2–3%) after functionalization. Thus, according to this TGA analysis, the amount of the polyamines covalently bonded to the MWNTs was estimated, based on the total weight of MWNTs-PA, to be about 40 wt

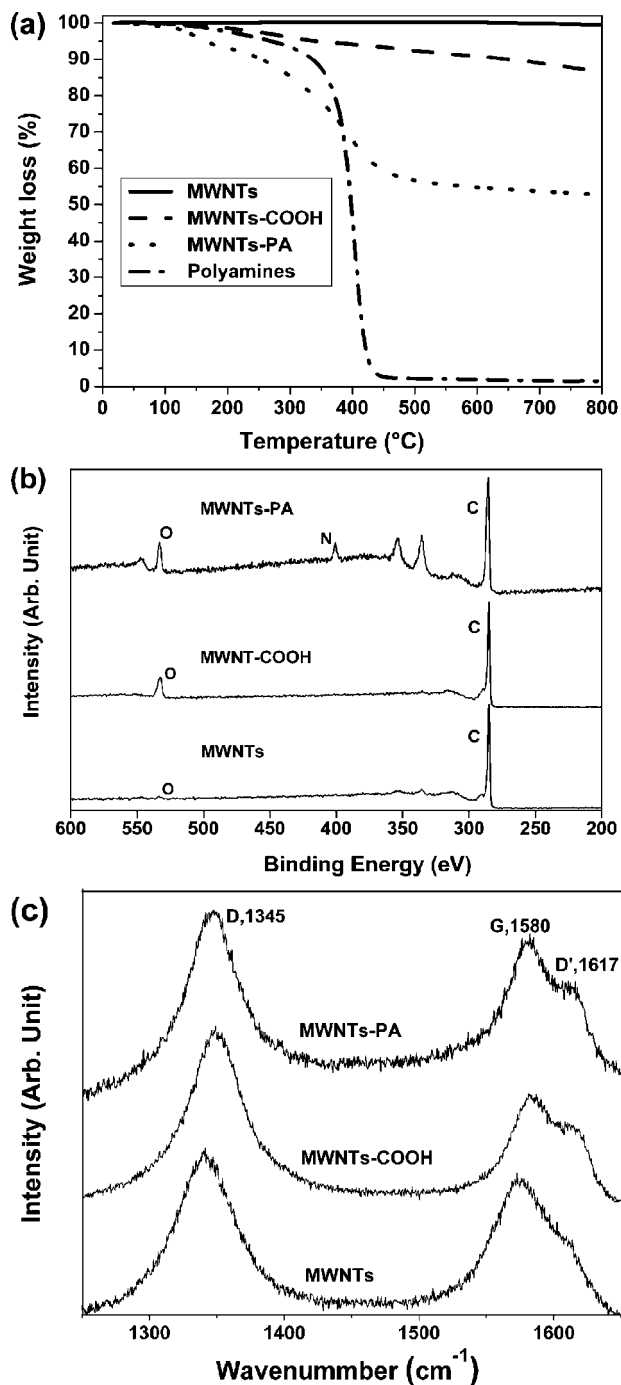


Figure 2. (a) TGA analysis, (b) X-ray photoemission survey spectra, and (c) Raman spectra of the pristine MWNTs, MWNTs-COOH, and MWNTs-PA.

Table 1. Element Analysis of MWNTs, MWNTs-COOH, MWNTs-PA, and Polyamines

| sample | C (%) | H (%) | N (%) |
|------------|-------|-------|-------|
| MWNTs | 92.33 | 0.09 | 0 |
| MWNTs-COOH | 81.28 | 0.48 | 0.3 |
| MWNTs-PA | 75.69 | 4.91 | 4.60 |
| polyamines | 70.77 | 9.27 | 12.30 |

%). The attachment of polyamines at the surface of MWNTs-PA was further confirmed by element analysis (Table 1). No nitrogen could be detected from the pristine MWNTs, and a small amount of nitrogen (0.3%) was observed for MWNTs-COOH due to the remaining impurities after the HNO_3 oxidation step. On the basis of Table 1, the nitrogen content (4.6%) of MWNTs-PA can also provide an estimation of the amount of

attached polyamine (around 40 wt %), which was comparable to the results of TGA analysis. Furthermore, the increase of hydrogen content of MWNTs-PA (4.91%) in comparison to that of MWNT-COOH (0.48%) may also provide the direct evidence for the grafting of polyamines. In addition, based on the assumption that all amino groups of the attached polyamines will react with carboxylic acid groups of MWNTs-COOH, the cross-link density of the functionalized MWNTs according to element analysis can be obtained from the ratio of amine number of polyamine and carboxylic acid number of MWNTs-COOH. As a result, around 60% carboxylic acid groups of MWNTs-COOH have been reacted into amide groups.

XPS was employed to determine the surface composition (in terms of elements present) of the MWNTs before and after functionalization (Figure 2b). After oxidation with strong acid, it is clear the increase of the intensity for the oxygen at 532 eV in the spectrum of MWNT-COOH compared to that of pristine MWNTs. No nitrogen could be found for pristine MWNTs and MWNT-COOH. However, a signal of nitrogen is observed at 400 eV in the spectrum of MWNTs-PA due to the presence of the polyamines at the surface of MWNTs-PA. From the relative intensities of the photoemission lines, the ratio of carbon, oxygen, and nitrogen for MWNTs-PA is 81%, 12%, and 7%, respectively. The nitrogen content in MWNTs-PA from XPS is consistent with the results from element analysis.

Raman spectroscopy is a widely used tool for studying structure, diameter, and electronic properties of carbon nanotubes.³³ As shown in Figure 2c, the disorder transition mode around 1345 cm^{-1} (D band) and characteristic tangential stretch mode peak at around 1580 cm^{-1} (G band) were observed for both pristine MWNTs, MWNTs-COOH, and MWNTs-PA. The D- to G-band intensity ratios (I_D/I_G) is typically taken as a measure standard of surface defects in carbon nanotubes.^{34,35} We found that this I_D/I_G ratio increases from 0.60 for the pristine MWNTs to 0.96 for MWNTs-COOH, which is an indication of the increment in the defects in the nanotube lattice after the strong acid treatment. It is worth noting that the D' band at 1617 cm^{-1} is hardly observed for pristine MWNTs but becomes more distinguishable for MWNTs-COOH, directly indicating an increase in the number of defects along the carbon nanotube wall after the oxidation.³⁶ The Raman spectrum of MWNTs-PA showed similar characteristic peaks compared to that of MWNTs-COOH. The I_D/I_G ratio of MWNTs-PA (0.93) remains virtually unchanged with respect to that of MWNT-COOH (0.96), which indicates that the electronic structure of the MWNTs-COOH is not perturbed by the covalent attachment of the polyamines.^{37,38}

Solubility. Because of a high density of amino functionalities along the backbone of the polyamines, the latter act as linkers for interconnecting or cross-linking the MWNTs as could be verified by the study of the dispersibility properties of the MWNTs in a variety of solvents (Figure 3). The pristine MWNTs (Figure 3a(1)) are not dispersible in water because of the tendency to assemble into aggregates or ropes due to the van der Waals interaction.⁵ After strong acid treatment and sonication, the dispersibility of MWNTs-COOH (Figure 3a(2)) was greatly improved in water, and no precipitation was observed at the bottom of the glass vial as reported in the literature.^{39–41} However, after reaction with the polyamines, the obtained MWNTs-PA (Figure 3a(3–8)) were not dispersible in any of the tested solvents after 30 min sonication, namely, deionized water, acid water (0.5 M HCl), DMF, THF, toluene, and CHCl_3 , while the pure polyamines are readily soluble in acidic water and the organic solvents mentioned here. Thus, the decrease in dispersibility after reaction clearly supports the fact that the polyamines were responsible for the cross-linking within or between the bundles of MWNTs. This is also in

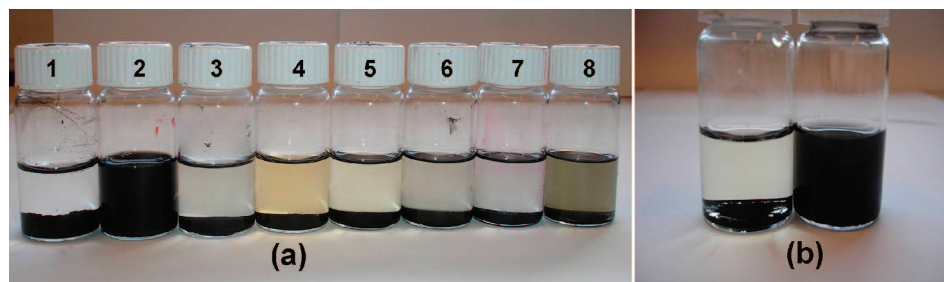


Figure 3. (a) Suspensions of MWNTs (1 mg/mL) in various solvent after 30 min sonication. Contents of glass vials, from left to right: (1) pristine MWNTs in water, (2) MWNT-COOH in water; from (3) to (8): MWNT-PA in deionized water, 0.5 M HCl water solution, DMF, THF, toluene, and CHCl_3 respectively. The images were taken after overnight storage. (b) Suspensions of MWNTs-PA (1 mg/mL) in water before hydrolysis (left) and after hydrolysis (right). The images were taken after 3 days storage.

analogy with what was reported in previous studies of the use of bifunctional nitrenes as linkers.²⁰ The de-cross-linking of MWNTs-PA by acid-catalyzed hydrolysis reaction was used to confirm the cross-linking of MWNTs-PA via formation of amide bonding.⁴² MWNTs-PA were treated in HCl water solution (2 M) under reflux for 3 days and then washed with deionized water until the pH was 7. After sonication for 30 min, MWNTs-PA could partially be redispersed in deionized water, as shown in Figure 3b. These results provide additional evidence for the amide linkage in the cross-linking process of the MWNTs.

SEM and TEM. The morphology and structure of pristine MWNTs, MWNTs-COOH, and MWNTs-PA were investigated by SEM. MWNTs-PA (micrograph shown in Figure 4c) present a major change in the morphology and structure in comparison to pristine MWNTs (micrograph in Figure 4a) and MWNT-COOH (micrograph in Figure 4b). While pristine MWNTs present a smooth surface and a loosely packed arrangement, the image of MWNTs-COOH shows not only that the length of nanotubes was greatly reduced by the strong acid treatment but also that the oxidized carbon nanotubes are highly tangled with each other and form matlike structure, called “bucky paper”.³⁰ By contrast, it is clear that the image of MWNTs-PA shows irregular blobs of material wrapped around the surface of the carbon nanotubes, resulting from the covalent attachment of the polyamines. It is quite difficult to identify the single carbon nanotubes, and some parts of the tubes are fully coated with polymers. Both randomly entangled structures and compact bundles of carbon nanotubes can be observed for MWNTs-PA. We assign this morphology to the covalent linkage of the bundles and the cross-linking of the MWNTs. Confirmation for this interpretation comes from TEM studies. The image of MWNTs-COOH (Figure 5a) shows that the acid-treated nanotubes have a rather smooth and clean surface without any extra phase adhering to and between them. In contrast, TEM pictures of MWNT-PA (Figure 5b–d) clearly show an irregular and discontinuous coating of an amorphous polymer layer around and between the carbon nanotubes and the interlinking of carbon nanotubes by the polymers. The polyamines can also act as bridge to interconnect or assemble carbon nanotubes into new configurations, mainly end-to-side (Figure 5c) and side-to-side (Figure 5d) junctions, which is potentially useful for the assembly of carbon-nanotube-based electronic devices.^{17–19}

Blends with Polyethylene. Carbon nanotubes are considered promising reinforcing materials for polymer composites which improve the mechanical, electrical, and thermal properties of polymers.^{43,44} However, cross-linked nanotubes might in principle display a lower processability as compared to the virgin ones. LDPE/MWNTs-PA composites were prepared by melt-blending of MWNTs-PA into LDPE using a microextruder to check whether the cross-linked MWNTs could be further processed into polymers. As shown in Figure 6, optical microscopy revealed a similar dispersion behavior of pristine

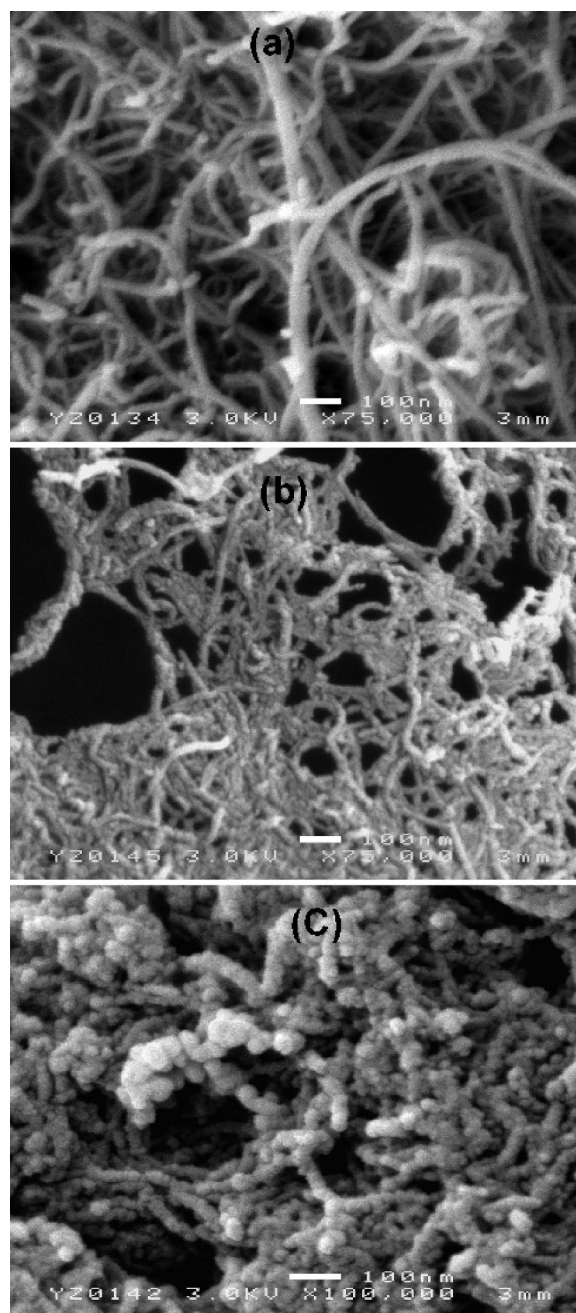


Figure 4. SEM images of (a) pristine MWNTs, (b) MWNTs-COOH, and (c) MWNTs-PA. The white bar represents 100 nm.

MWNTs and MWNTs-PA in the LDPE matrix. However, big clusters or clumps with the diameter up to 50 μm (black spot

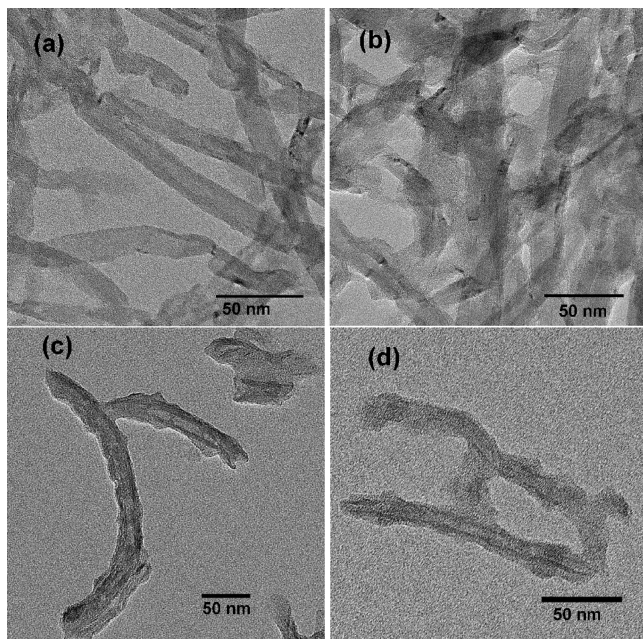


Figure 5. TEM images of (a) MWNTs-COOH and (b–d) MWNTs-PA.

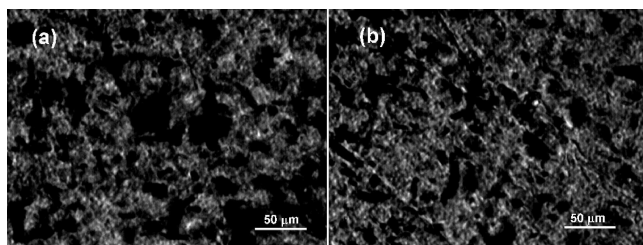


Figure 6. Optical micrograph of thin films of (a) LDPE/MWNTs composites (1 wt % MWNTs) and (b) LDPE/MWNTs-PA composites (1 wt % MWNTs-PA).

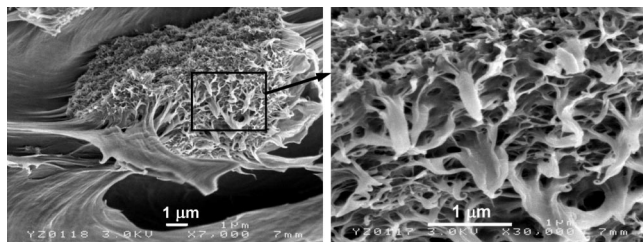


Figure 7. SEM image of the cluster surface of the LDPE/MWNT-PA composites (2 wt % MWNTs-PA).

in Figure 6) of carbon nanotubes can be found in both polymer composites. Nevertheless, a more homogeneous distribution of the polyamine-cross-linked nanotubes clusters can be observed (Figure 6b). It seems that the mechanical energy in the melt blending process is not enough to overcome the van der Waals interaction between carbon nanotubes, which is also main disadvantage of the use of melt blending process as dispersion techniques.^{43,44} It is believed that the reinforcing ability of nanotubes will be lower when carbon nanotubes are dispersed poorly into polymer matrix. The presence of big clusters of the MWNTs-PA embedded in the LDPE matrix is also confirmed by SEM micrographs of the fracture surface of the LDPE/MWNTs-PA composites after mechanical testing (left of Figure 7). Failure only occurred within the PE matrix, and the carbon nanotubes are difficult to distinguish due to the coating or wrapping of the carbon nanotubes by the LDPE at the surface

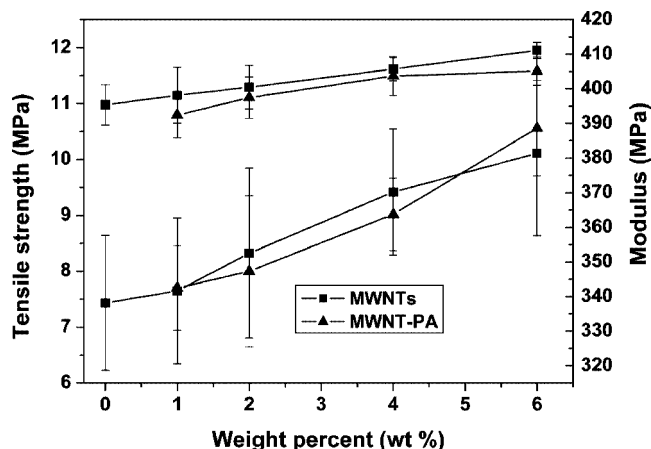


Figure 8. Mechanical properties of LDPE/MWNTs and LDPE/MWNT-PA composites at a function of carbon nanotube loading.

of the cluster (right of Figure 7). Tensile measurements of the LDPE/MWNTs and LDPE/MWNTs-PA composites presented in Figure 8 reveal similar mechanical properties for different loading of carbon nanotubes in the range from 1 to 6 wt %. Compared with the neat LDPE, tensile strength of both types of composites remained almost unchanged with the increase of MWNTs content, and the presence of the carbon nanotubes leads to a slightly increase in Young's modulus. These results are similar to what is reported in the literature⁴⁵ for PE/MWNTs composites prepared by the melt blending and indicate that both the processability and reinforcing ability of the carbon nanotubes as filler for the LDPE are retained after cross-linking with the polyamines. However, the enhancement on mechanical property of the LDPE matrix when using the cross-linked MWNTs as fillers is not realized due to poor dispersion of the fillers when using the melt blending. Other methods, e.g. solution blending, use of surfactants may be required in order to efficiently disperse MWNTs in a polymer matrix.

Conclusions

We report a simple novel approach to cross-link multiwalled carbon nanotubes (MWNTs) by using polyamines synthesized from alternating polyketones. The covalent attachment of the polyamines on the MWNTs is confirmed by TGA, XPS, Raman spectra, and element analysis. It is found that around 40 wt % polyamines is grafted into the surface of the MWNTs. The cross-linked MWNTs display poor solubility in water and several other organic solvents. The polymer bridges within as well as between the bundles of the MWNTs after cross-linking were clearly observed by TEM. No detrimental effects on the processability of the nanotubes as well as on the mechanical properties of the composites were found when melt blending the cross-linked MWNTs into a LDPE matrix. The cross-linked MWNTs may find applications in electronic circuits or in reinforcing materials for polymer nanocomposites. In contrast to low molecular weight cross-linking agents (such as diamines), the use of a polymeric material might open new processing possibilities for interconnected MWNTs.

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